Reconstruction of seasonal temperature variability in the tropical Pacific Ocean from the shell of the scallop, Comptopallium radula

Julien Thébault, Laurent Chauvaud, Jacques Clavier, Jennifer Guarini, Robert B. Dunbar, Renaud Fichez, David A. Mucciarone, Eric Morize

The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

Reconstruction of seasonal temperature variability in the tropical Pacific Ocean from the shell of the scallop, *Comptopallium radula*

JULIEN THÉBAULT,[1,*] LAURENT CHAUVAUD,[2] JACQUES CLAVIER,[2] JENNIFER GUARINI,[3] ROBERT B. DUNBAR,[4] RENAUD FICHEZ,[5] DAVID A. MUCCIARONE,[4] and ERIC MORIZE[6]

(1) IRD, Unité de Recherche Camélia, BP A5, 98848 Nouméa Cedex, New Caledonia

(2) IUEM-UBO, UMR CNRS 6539, Place Nicolas Copernic, 29280 Plouzané, France

(3) Observatoire Océanologique de Banyuls, Université Pierre et Marie Curie, UMR CNRS 7621, 66650 Banyuls-sur-Mer, France

(4) Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA

(5) Centre d'Océanologie de Marseille, Station Marine d'Endoume, Rue de la Batterie des Lions, 13007 Marseille, France

(6) Centre IRD de Bretagne, US Chronos, BP 70, 29280 Plouzané, France

Running head: Scallop shells as temperature recorders in the Pacific Ocean

* Corresponding author. Present address: IUEM-UBO, UMR CNRS 6539, Place Nicolas Copernic, 29280 Plouzané, France. *E-mail*: julien.thebault@univ-brest.fr

The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

ABSTRACT

We investigated the oxygen isotope composition ($\delta^{18}O$) of shell striae from juvenile *Comptopallium radula* (Mollusca; Pectinidae) specimens collected live in New Caledonia. Bottom-water temperature and salinity were monitored in-situ throughout the study period. External shell striae form with a 2-day periodicity in this scallop, making it possible to estimate the date of precipitation for each calcite sample collected along a growth transect. The oxygen isotope composition of shell calcite ($\delta^{18}O_{shell\ calcite}$) measured at almost weekly resolution on calcite accreted between August 2002 and July 2003 accurately tracks bottom-water temperatures. A new empirical paleotemperature equation for this scallop species relates temperature and $\delta^{18}O_{shell\ calcite}$:

$$t(°C) = 20.00(\pm0.61) - 3.66(\pm0.39) \times (\delta^{18}O_{shell\ calcite\ VPDB} - \delta^{18}O_{water\ VSMOW})$$

The mean absolute accuracy of temperature estimated using this equation is 1.0 °C at temperatures between 20 and 30 °C. Uncertainties regarding the precise timing of $CaCO_3$ deposition and the actual variations in $\delta^{18}O_{water}$ at our study sites probably contribute to this error. Comparison with a previously published empirical paleotemperature equation indicates that *C. radula* calcite is enriched in ^{18}O by ~0.7 ‰ relative to equilibrium. Given the direction of this offset and the lack of correlation between shell growth rate and $\delta^{18}O_{shell\ calcite}$, this disequilibrium is unlikely to be related to kinetic isotope effects. We suggest that this enrichment reflects (1) a relatively low pH in the scallop's marginal extrapallial fluid (EPF), (2) an isotopic signature of the EPF different from that of seawater, or (3) Rayleigh fractionation during the biocalcification process. Relative changes in $\delta^{18}O_{shell\ calcite}$ reflect seawater temperature variability at this location and we suggest that the shell of *C. radula* may be useful as an archive of past seawater temperatures.

 doi: 10.1016/j.gca.2006.10.017

1. INTRODUCTION

Paleoclimate archives are important tools for understanding the causes of climate change and for the validation of climate models (Dunbar and Cole, 1999). In most climate models, sea surface temperature (SST) is an important variable because of its correlation with and control of other climate parameters such as atmospheric moisture content and temperature, rainfall, and heat flux. The known spatial heterogeneity of climatic response to changes in radiative forcing suggests a need for well-calibrated paleoclimate records from diverse geographic settings.

The oxygen isotope ratio ($^{18}O/^{16}O$) of marine biogenic carbonate is controlled by temperature and the oxygen isotope composition of the seawater from which it precipitates (McCrea, 1950; Epstein et al., 1953). Oxygen isotope paleothermometry has been employed in a number of studies of Cenozoic marine molluscs (Krantz et al., 1987; Andreasson and Schmitz, 1996; Bice et al., 1996; Andreasson and Schmitz, 1998; Kirby et al., 1998; Andreasson and Schmitz, 2000; Hickson et al., 2000; Tripati et al., 2001; Dutton et al., 2002) because their shells grow by periodic accretion of calcite or aragonite (Pannela and McClintock, 1968). This characteristic provides a means of assigning calendar dates to each successive band of accreted shell material, assuming that the periodicity of accretion is known. Using improved micro-sampling and micro-analytical techniques, several recent studies have demonstrated that rapidly growing bivalve mollusc shells contain high resolution proxy records of seawater temperature (Kennedy et al., 2001; Elliot et al., 2003; Chauvaud et al., 2005).

In this study, we compare in-situ instrumental seawater temperature with the oxygen isotope composition of shell calcite from six juvenile scallops (*Comptopallium radula,* L., 1758) from the southwest lagoon of New Caledonia (Fig. 1a). *C. radula* is a large (H_∞ = 92.4 mm; Lefort, 1994) sedentary scallop that lives under branching corals or on coralline fragment beds, generally between 0.5 and 5 m depth, in the tropical Indo-West Pacific Ocean. As in many other scallop species, the shell surface of *C. radula* is textured with concentric striae (Fig. 1b). Marking experiments using calcein fluorescent dye have demonstrated that one stria is formed every two days (Thébault et al., 2006). We have now measured the oxygen isotope composition

 doi: 10.1016/j.gca.2006.10.017

of carbonate samples collected along shell growth transects to develop an empirical temperature equation which is then compared with some previous $\delta^{18}O$:temperature relationships calibrated for inorganically precipitated calcite and other molluscs.

Most previous paleotemperature records from this region are derived from elemental and isotopic ratios in scleractinian corals (Beck et al., 1992; Quinn et al., 1996a,b; Quinn et al., 1998; Quinn and Sampson, 2002; Watanabe et al., 2003; Corrège et al., 2004; Kilbourne et al., 2004). Our dataset contributes to the relatively small number of oxygen isotope studies on scallop species (Krantz et al., 1984; Krantz et al., 1987; Tan et al., 1988; Hickson et al., 2000; Owen et al., 2002a,b; Chauvaud et al., 2005) and allows the evaluation of the potential of *C. radula* for paleoclimatic studies.

2. METHODS

2.1. Study area

New Caledonia is located in the southwest Pacific Ocean, between 19-23°S and 163-168°E (Fig. 2). The main island, Grande Terre, is surrounded by an 1100 km long barrier reef. The southwest lagoon covers 2066 km² and has an average depth of 21 m. Our study sites near Nouméa are Sainte-Marie Bay (22°18′22″S, 166°28′89″E) and Koutio Bay (22°13′45″S, 166°25′33″E). Both sites are shallow (< 5 m depth) with muddy sandy sediment. Bottom-water temperatures and salinities were measured from August 7, 2002 to August 1, 2003. Temperatures were recorded hourly using a EBRO EBI-85A thermal probe fixed to a bottom mooring (accuracy ±0.1 °C). Salinity (average of the first meter of the water column above the seafloor) was measured weekly using a SeaBird SBE19 CTD profiler, and is reported using the Practical Salinity Scale. Salinity data were interpolated linearly to obtain daily values.

Because salinity and $\delta^{18}O_{water}$ are positively correlated (Craig and Gordon, 1965), the oxygen isotope composition of water was measured at twelve sampling sites along a salinity gradient in the Dumbéa River (Fig. 2) at the beginning of the 2003 dry season (normal river

flow). The $\delta^{18}O_{water}$ analyses were performed using a modification of the standard CO_2-H_2O ^{18}O isotope equilibration technique (Epstein and Mayeda, 1953). For each sample, 2.4 mL of water were equilibrated for 6 h in a reaction vessel with CO_2 at 880 mbar and 21 °C. A cold trap at -80 °C was used to remove water and the resultant CO_2 was frozen onto a cold finger prior to analysis on a Europa SIRA II dual-inlet isotope ratio mass spectrometer. The internal standard used was North Sea Water ($\delta^{18}O$ = -0.20 ‰ VSMOW). Analytical precision was 0.06 ‰ (1σ). All samples were run in duplicate and data are reported in ‰ with respect to VSMOW. Salinity was measured using a Guildline 8410A Portasal inductive salinometer (accuracy ±0.002), calibrated with IAPSO Standard Seawater (Ocean Scientific International Ltd., Petersfield, UK). Three samples were measured in triplicate with an average standard deviation of 0.008.

2.2. Scallop sampling, preparation, and analysis

Comptopallium radula grows rapidly, especially during the first two years of life (Lefort, 1994). After sexual maturity is achieved during the third year (Lefort and Clavier, 1994), the annual shell growth rate drops. For this study only juvenile scallops were analysed because they have the largest annual increase in shell size (compared with mature specimens) and provide the highest temporal resolution in carbonate records.

Six live juvenile *C. radula* specimens (maximum shell height = 69.2 mm) were collected by SCUBA diving at the beginning of the 2003 cool season. In Sainte-Marie Bay, shell SM1 was collected on June 23, shell SM2 on July 1, and shell SM3 on July 13. In Koutio Bay, shell BK1 was harvested on May 21, shell BK2 on June 14, and shell BK3 on July 2. After collection, the scallops were immediately killed and their shells cleaned by soaking in 90 % acetic acid for 45-60 s to remove bio-fouling, and then rinsed with distilled water and air-dried.

Shell samples (n = 225; 34 to 40 samples per shell) for isotopic analyses were collected (using a hand-held micro-drill equipped with a 0.6-mm engraving bit) along a transect line perpendicular to the striae, from the umbo to the ventral margin (Fig. 1b). Drilling was restricted to the ridges of the striae to ensure that shell material was not cross-contaminated by

mineralogically different layers of $CaCO_3$. Because the distance between two successive striae is not constant, each sample contained material from 2 to 5 striae (average = 2.3 striae/sample), and was separated from the next sample by 1 to 3 striae (average = 1.2 striae). Given the 2-day periodicity of striae formation (Thébault et al., 2006), this sampling scheme means that each sample corresponds approximately to 7 days of growth.

Aliquots of shell calcite weighing between 32 and 212 µg (mean = 88 µg) were acidified in 100 % phosphoric acid at 70 °C for 470 s and analyzed using an automated Finnigan MAT Kiel III carbonate device coupled to a Finnigan MAT 252 isotope ratio mass spectrometer at Stanford University. Shell isotopic data are expressed in conventional delta (δ) notation (Epstein et al., 1953) relative to the VPDB standard. A total of 25 samples of the international isotopic reference standard NBS-19 (mean weight of standard aliquots = 83 µg) and 15 samples of the Stanford Isotope Lab Standard SLS-1 (mean weight = 84 µg) were analyzed with the scallops and yielded a reproducibility (1σ) of 0.049 ‰ VPDB (NBS-19) and 0.051 ‰ VPDB (SLS-1) for $\delta^{18}O$, and 0.029 ‰ VPDB (NBS-19) and 0.035 ‰ VPDB (SLS-1) for $\delta^{13}C$.

A date of formation was assigned to each sample drilled from all shells (except SM2) by backdating from the outer most stria (i.e., harvest date), based on the 2-day periodicity of striae formation in juvenile *C. radula* (Thébault et al., 2006). A different method was used for shell SM2 because of a clearly visible hiatus in shell growth on its external surface. This growth hiatus corresponds to a period during which shell growth ceased. The date of growth cessation and the duration of the interval of zero growth were, however, unknown. The method we used for shell SM2 is based on the very small inter-individual variability of $\delta^{18}O_{shell\ calcite}$ profiles in *C. radula*. First, all samples collected between the ventral margin and the growth hiatus were dated using the method described for the 5 other shells (time-anchored part of the SM2 $\delta^{18}O$ profile - absolute chronology). Then, each sample collected between the growth hiatus and the umbo was dated in relation to the next one, based on the periodicity of striae formation (time-unanchored part of the SM2 $\delta^{18}O$ profile - relative chronology). Finally, this time-unanchored part of the SM2 $\delta^{18}O$ profile was time correlated with the mean $\delta^{18}O$ profile calculated from the other 5

 doi: 10.1016/j.gca.2006.10.017

shells, allowing us to determine the absolute chronology of the dataset (synchronization involved the maximization of the correlation coefficient between these two datasets). This method permits the estimation of the date of growth cessation as well as the duration of the interval of zero growth.

An estimate of shell growth rate, based on the periodicity of striae formation, was made for each shell by measuring distances between successive striae (growth increment width) using an image analysis technique described in detail by Chauvaud et al. (1998). The estimated growth rates are expressed in $\mu m\, 2d^{-1}$. In this paper, we define "shell growth rate" as the dorso-ventral linear extension of the shell per unit time. Since this does not take into account ontogenetic changes in shell thickness, growth rate is likely to differ from absolute calcification rate (see Gillikin et al. (2005) for a helpful discussion).

The outer layer of scallop shells was found to be composed of pure foliated calcite (Roux et al., 1990; Barbin et al., 1991). Nevertheless, we checked the mineralogy of the striae we sampled using an X-ray powder diffractometer equipped with an INEL curved position-sensitive detector (CPS120) and a graphite monochromator, using $CoK_{\alpha 1}$ radiation at 35 mA and 30 kV.

2.3. Calibration of the $\delta^{18}O$:temperature relationship

As described in section 2.2, the $\delta^{18}O$ value of each sample represents an average of ~5 days growth (~2.3 striae). To match this isotopic time averaging, 5-day moving averages of temperature and interpolated weekly salinity measurements were calculated for the calibration. Ordinary Least Squares (OLS) regression was used to examine the $\delta^{18}O$:temperature relationship, by expressing $\delta^{18}O$ as the isotopic difference between shell calcite and seawater:

$$t = A + B \times (\delta^{18}O_{\text{shell calcite}} - \delta^{18}O_{\text{water}}) , \quad (1)$$

where t is temperature (°C), *A* and *B* are constants, and $\delta^{18}O_{shell\ calcite}$ and $\delta^{18}O_{water}$ are expressed in ‰ relative to VPDB and VSMOW, respectively. A "comparison of regression lines" procedure (Statgraphics Centurion XV statistical software) was used to test whether there were significant differences between the slopes of the OLS regressions calculated for each of the six shells, and between the slopes of the OLS regressions calculated for each of the two study sites.

This relationship was then compared to previous paleotemperature equations established for other calcitic molluscs (Epstein et al., 1953; Owen et al., 2002a; Chauvaud et al., 2005) and for inorganically precipitated calcite (Kim and O'Neil, 1997). In the equation of Epstein et al. (1953), later modified by Craig (1965), both calcite and water oxygen isotope data are relative to the same working standard of the mass spectrometer used in the early days at the University of Chicago, i.e., CO_2 from PDB. Water analyses normalized to the VSMOW scale and carbonates normalized to the VPDB scale cannot be used in this equation. However, it was rewritten by Sharp (2006) in a form appropriate for calcite and water oxygen isotope data expressed relative to VPDB and VSMOW, respectively. The equation of Owen et al. (2002a) was also rewritten in a form suitable for comparison, considering the whole of their dataset (i.e., 31 data points instead of 22 in their equation). To allow comparison with our linear relationship, the equation of Kim and O'Neil (1997) was modified from the form $10^3 \ln\alpha = A(10^3\ T^{-1}) + B$, and was approximated by a least squares linear regression following conversion of their $\delta^{18}O_{calcite}$ data to the VPDB scale. Calcite oxygen isotope data reported on the VSMOW scale in their study were first corrected (+0.25 ‰) to account for differences between the acid fractionation factor they used (1.01050) and the one commonly accepted for the reaction of carbonate with H_3PO_4 at 25 °C (1.01025). These data were then converted to the VPDB scale using the equation of Coplen et al. (1983). The coefficients of these four paleotemperature equations are reported in Table 1.

 doi: 10.1016/j.gca.2006.10.017

3. RESULTS

3.1. Hydrologic survey

From August 2002 to August 2003, the average daily bottom-water temperature ranged from 20.4 to 29.3 °C in Sainte-Marie Bay, and from 20.1 to 29.7 °C in Koutio Bay. The mean diurnal temperature range was 0.6 °C in Sainte-Marie Bay and 0.9 °C in Koutio Bay, with maximum amplitudes of 1.7 and 1.9 °C, respectively. Bottom-water salinity ranged from 34.73 to 36.18 in Sainte-Marie Bay, and from 33.43 to 36.52 in Koutio Bay. The water oxygen isotope composition showed a linear co-variation with salinity over the range 2.33-34.68. The relationship between $\delta^{18}O_{water}$ and salinity based on a least squares regression equation (n = 12, $r^2 = 0.999$, $p < 0.001$) was:

$$\delta^{18}O_{water\ VSMOW} = 0.168(\pm 0.003)\ S - 5.068(\pm 0.08)\ , \quad (2)$$

Quoted errors on the slope and intercept are the 95 % confidence intervals. Extrapolating this linear relationship to a salinity of 36.52 yields a $\delta^{18}O_{water}$ annual range of 0.24 ‰ in Sainte-Marie Bay and 0.52 ‰ in Koutio Bay.

3.2. Mineralogy, shell growth rate and $\delta^{18}O_{shell\ calcite}$

X-ray diffractograms obtained from powder samples of the shell of *C. radula* unambiguously indicated that striae are composed of calcite. Nevertheless, as XRD is a bulk detection method, we cannot unequivocally state that striae do not contain small amounts of aragonite or magnesium carbonate.

The oxygen isotope composition of shell calcite, shell growth rate estimates, and bottom-water temperature are superimposed for each shell in Fig. 3. For all specimens, except SM2, it was not possible to reconstruct growth curves for portions of the shells accreted before

August 2002 because of striae abrasion in the oldest parts of the shells. The average shell growth rate was 263 µm $2d^{-1}$ with maximum values on the order of 450 µm $2d^{-1}$. There is little similarity between the six growth rate profiles, and no clear seasonal cycle of growth. Moreover, the isotopic record from shell SM2 indicates a growth stop for ca. 2.5 months during the Summer of 2002-2003.

The oxygen isotope composition of shell calcite ranged from -1.47 to 0.28 ‰ VPDB (Fig. 3). Isotopic profiles of the six shells show similar variations in 2002-2003. In order to determine the influence of temperature, salinity and shell growth rate on $\delta^{18}O_{shell\ calcite}$, the $\delta^{18}O$ data were fit to a multivariate model of these variables (Table 2). Considering that the *p*-value for shell growth rate was 0.365 (i.e., $p > 0.01$), this term was not statistically significant and the model was therefore simplified. The best multiple linear regression model incorporated only salinity and temperature. In this model, however, salinity explained only 0.46 % of the variation in $\delta^{18}O_{shell\ calcite}$. Our model also revealed the existence of a statistically significant effect of the interaction "temperature*salinity".

3.3. Calibration of the paleotemperature equation

To develop a paleotemperature equation, we used *C. radula* $\delta^{18}O_{shell\ calcite}$, and 5-day moving averages of daily temperature and $\delta^{18}O_{water}$ (calculated from salinity measurements). The resulting linear relationship ($n = 225$, $r^2 = 0.609$, $p < 0.001$, Fig. 4) is:

$$t(°C) = 20.00(\pm 0.61) - 3.66(\pm 0.39) \times (\delta^{18}O_{shell\ calcite\ VPDB} - \delta^{18}O_{water\ VSMOW}) , \quad (3)$$

Quoted errors on the slope and intercept are the 95 % confidence intervals. This equation was then used with the $\delta^{18}O_{shell\ calcite}$ values of the six scallops to predict the temperature at which the $CaCO_3$ samples precipitated. The mean absolute error (MAE) shows the accuracy of the temperature prediction to be 1.0 °C.

 doi: 10.1016/j.gca.2006.10.017

The $\delta^{18}O$:temperature relationships calculated for each of the six shells are presented in Table 3. All relationships were highly significant ($p < 0.001$), with r^2 ranging from 0.490 to 0.764, and MAE ranging from 0.8 to 1.2 °C. The test for comparison of slopes reveals that there is no significant difference between the slopes calculated (1) for each of the six shells ($p = 0.447$), (2) for the three shells of Sainte-Marie Bay ($p = 0.589$), and (3) for three shells of Koutio Bay ($p = 0.331$). Moreover, this test shows that the slope of the $\delta^{18}O$:temperature relationship is not significantly different for the two study sites ($p = 0.127$). These results indicate that each specimen preserved similar information, a strong argument in support of the validity of this proxy.

The *C. radula* $\delta^{18}O$:temperature relationship predicts higher temperatures relative to estimates from paleotemperature equations commonly used over the range 20-30 °C (Fig. 5). Our $\delta^{18}O_{shell\ calcite}$ data lie above the equilibrium line (as defined by the equation of Kim and O'Neil (1997) for $[HCO_3^-] = 5$ mM) by, on average, 0.73 ‰, equivalent to a temperature differential of about -3.6 °C. The slope of our equation compares favourably with the slopes of the relationships calibrated by Owen et al. (2002a) and Chauvaud et al. (2005) on the Great Scallop *Pecten maximus* (tests for comparison of slopes: $p = 0.229$ and 0.903, respectively). It is, however, statistically different from the slope of Kim and O'Neil (1997) equation ($p < 0.001$).

4. DISCUSSION

4.1. Accuracy and limits of the temperature prediction

Using radioisotope measurements in the shell of the scallop, *Argopecten irradians*, Wheeler et al. (1975) found that the rate of mineral deposition was lower in the evening than at midday. Moreover, the timing of striae formation in this species was shown to be influenced by the photoperiod, with striae forming primarily in late afternoon and evening (Wrenn, 1972). Nothing is known about the timing of this process in *Comptopallium radula*. Although the time

resolution of our oxygen isotope analyses is high (each $\delta^{18}O_{shell\ calcite}$ value represents an average of 4.6 days of $CaCO_3$ precipitation), if calcification does not take place throughout the day then using average daily temperature values for the calibration of the equation can lead to errors as large as ±0.30 °C in Sainte-Marie Bay and ±0.45 °C in Koutio Bay. The sum of errors associated with the diurnal temperature amplitude, our 5-day averaging procedure, and the accuracy of the thermal probe (±0.1 °C), can explain nearly half (0.5 °C) of the 1.0 °C uncertainty of the temperature prediction. To proceed further with the use of isotopic signatures as environmental proxies, studies on the timing of $CaCO_3$ deposition, in addition to better micro-analytical techniques at the scale of individual striae, are necessary.

It is also possible that the low sampling frequency for salinity (weekly measurements) was insufficient and induced an unknown amount of error. This is highlighted by a slightly greater mean absolute error for shells harvested from Koutio Bay, a site that experiences greater freshwater inputs and therefore more variable salinity (Table 3). Sea surface salinity (SSS) was measured from 1995 to 2003 at near-daily resolution close to Nouméa (ZoNeCo programme, "Variability of surface thermohaline structures in the New Caledonian Exclusive Economic Zone"). This dataset reveals occasional significant decreases in salinity (down to 28.9) on a sub-weekly basis following storms (characterized by large rainfall and elevated river runoff for 1 or 2 days). If such salinity decreases occurred during our study, they may have been missed by our weekly sampling scheme, leading to errors in the estimation of the oxygen isotope composition of seawater used in the calibration equation.

A surprising result of our study is the weak influence of salinity on $\delta^{18}O_{shell\ calcite}$ (Table 2). According to Eq. (2), salinity variations should generate annual ranges in $\delta^{18}O_{water}$ of 0.24 to 0.52 ‰ depending on the study site, which represents 14 to 30 % of the annual range in $\delta^{18}O_{shell\ calcite}$. Therefore, it is astonishing that in our model salinity explains only 0.46 % of the variability of $\delta^{18}O_{shell\ calcite}$. The actual $\delta^{18}O_{water}$:salinity relationship, however, may be different from Eq. (2) if salinity variations at our study sites result from a balance between evaporation and precipitation rather than dilution by river water. Moreover, $\delta^{18}O_{water}$:salinity relationships

can be temporally variable on short timescales (Rohling and Bigg, 1998). Hence, the real annual range in $\delta^{18}O_{water}$ may be different from the one calculated from Eq. (2). Temperature is, by far, the dominant factor controlling the shell oxygen isotope composition and this predominance, in addition to the existence of a significant effect of the "temperature*salinity" interaction (Table 2), may make it harder to identify the magnitude of a “salinity” effect. Nevertheless, we suggest that salinity-induced change in $\delta^{18}O_{water}$ is not a major contributor to the $\delta^{18}O_{shell\ calcite}$ record, as previously proposed by Quinn et al. (1996b) in their study on a massive coral from the southwest lagoon of New Caledonia.

4.2. Explanations for the observed fractionation

Temperature reconstruction using molluscs is often considered straightforward by virtue of a longstanding assumption that the partitioning of oxygen isotopes between seawater and mollusc shells closely follows the isotopic equilibrium observed between inorganically precipitated calcium carbonate and water. Although this has been confirmed in a number of molluscs (Epstein et al., 1953; Kirby et al., 1998; Surge et al., 2001; Elliot et al., 2003), and in a scallop species (Chauvaud et al., 2005), other studies have reported disequilibrium precipitation of scallop shell calcite (Mitchell et al., 1994; Owen et al., 2002a,b). The variety of fractionation patterns observed implies that species-specific assessments must be completed. This is highlighted by the differences in the equations presented in Fig. 5. Discrepancies between mollusc records and their interpretations often arise from a lack of knowledge of the basic biology and ecology (growth rate, seasonal timing, and duration of growth) of the molluscan species used as environmental recorders.

We compared our $\delta^{18}O_{shell\ calcite}$ values with those predicted by the Kim and O’Neil (1997) empirical equation, which is the most recent approximation for equilibrium partitioning of oxygen isotopes between inorganic calcite and seawater. Our results indicate that *C. radula* calcite is enriched in ^{18}O by ~0.73 ‰ with respect to inorganic calcite precipitated in equilibrium with water. Deviation from isotopic equilibrium in biogenic carbonates has been

328 explained historically in terms of "vital effects" (Urey, 1947) which include a combination of
329 kinetic and metabolic effects (McConnaughey, 1989). Kinetic effects, inferred from a
330 simultaneous depletion in ^{18}O and ^{13}C and a linear correlation between skeletal $\delta^{18}O$ and $\delta^{13}C$,
331 have been observed at high calcification rates in the carbonate skeletons of some organisms
332 (McConnaughey, 1989). A weak but statistically significant $\delta^{18}O$:$\delta^{13}C$ linear relationship is
333 observed when data from the 6 scallops are pooled (n = 225, r^2 = 0.206, p < 0.001; Fig. 6).
334 However, if kinetic effects associated with high *C. radula* calcification rates had occurred, we
335 would have measured lower $\delta^{18}O$ values than predicted by the Kim and O'Neil (1997) equation.
336 In addition, no significant relationship was found between $\delta^{18}O_{shell\ calcite}$ and shell growth rate
337 (Table 2).

338 Kim and O'Neil (1997) observed that the extent of isotopic fractionation between water
339 and calcite increased with increasing initial concentration of bicarbonate ions at any given
340 temperature. They concluded that calcites precipitated from solutions of varying [HCO_3^-] were
341 forming out of oxygen isotopic equilibrium with water since there should be only one
342 equilibrium fractionation factor between calcite and water at any temperature. Spero et al.
343 (1997) have shown that $\delta^{13}C$ and $\delta^{18}O$ values of calcitic shells of living planktonic foraminifera
344 decrease as seawater [CO_3^{2-}] (or pH) increases. Zeebe (1999) suggested that the disequilibrium
345 precipitation described by Kim and O'Neil (1997) may be explained by multiple equilibrium
346 fractionations at a constant temperature but different pH values. Zeebe (1999) estimated that the
347 pH of the solution resulting in the equation of Kim and O'Neil (1997) was 7.8 and that an
348 increase in seawater pH by 0.1 unit produces a decrease of 0.11 ‰ in $\delta^{18}O_{calcium\ carbonate}$.

349 Two other recent studies found that the $\delta^{18}O_{shell\ calcite}$ of the scallop *Pecten maximus*
350 exhibited enrichment relative to equilibrium (as determined by the Kim and O'Neil (1997)
351 equation) in both laboratory (+0.6 ‰; Owen et al., 2002a) and field experiments (+0.4 ‰;
352 Owen et al., 2002b). Our observed +0.73 ‰ enrichment is in good agreement with results of
353 these two studies. Using Zeebe's model, the fractionation we measured in *C. radula* may be
354 explained by a pH of ~7.14 in the extrapallial fluid (EPF) where shell calcification actually
355 takes place. Analyses of marine bivalve EPF have shown its chemistry is significantly different

from that of seawater. The pH of EPF was measured in many marine bivalve species, with most values lying between 7.3 and 7.5, i.e., lower than in the external medium (for example, seawater at pH 7.9 to 8.2; Crenshaw, 1972; Wada and Fujinuki, 1976). This lowered pH is consistent with biomineralization models that assume the EPF is isolated from ambient seawater and that exchanges between this compartment and the external medium through the periostracum are limited, such as in the general model of molluscan shell calcification proposed by Wilbur and Saleuddin (1983). Therefore, the enrichment observed in the shell of *C. radula* could be related to low pH in the EPF compared to the pH in the experiment of Kim and O'Neil (1997), more than to vital effects.

According to Kim et al. (2006), however, Zeebe's model may be invalid and the isotopic fractionation between carbonate (aragonite and witherite) and water is independent of pH. Therefore, we suggest that the offset from equilibrium we observed may result from an isotopic signature of the EPF different from that of seawater, or by some kind of Rayleigh fractionation. The latter process occurs in a closed system or a finite reservoir when a chemical reaction fractionates isotopes and the reaction products are removed from the system or do not back-react. This results in a shift of the oxygen isotope composition of both the reactant and the product of the reaction. Rayleigh fractionation has been well described for changes in the $\delta^{18}O$ of water and vapour during evaporation where the vapour is continuously removed (i.e., isolated from the water) with a constant fractionation factor (Kendall and Caldwell, 1998). This process may occur during biocalcification of the shell of *C. radula* as (1) exchanges between the external medium and the extrapallial compartment are limited (semi-closed system; see Wilbur and Saleuddin, 1983), limiting the pool of HCO_3^- ions required by the reaction, and (2) the product of this reaction (i.e., calcite) does not back-react. If the effects of Rayleigh fractionation manifest themselves in the oxygen isotope system, they will result in ^{18}O enrichment in both the HCO_3^- reservoir and the precipitated calcite, as previously suggested by Mickler et al. (2004) to explain the offset from equilibrium they observed in modern tropical speleothems.

 doi: 10.1016/j.gca.2006.10.017

383 **4.3. Conclusions**

384

385 This study highlights the potential use of shells as high resolution archives of seawater
386 temperature in New Caledonia. Our new $\delta^{18}O$:temperature relationship permits the
387 reconstruction of seasonal SST variations within ±1.0 °C over the temperature range 20-30 °C.
388 Accuracy could be improved with better knowledge of the timing of striae formation and with
389 salinity measurements at higher temporal resolution. We suggest that an observed 0.73 ‰ offset
390 between the *C. radula* $\delta^{18}O$:temperature relationship and a recent equation describing isotopic
391 equilibrium in inorganic calcite grown in seawater may be caused by (1) differences in solution
392 pH between the scallop's extrapallial fluid and seawater, (2) an isotopic signature of the EPF
393 different from that of seawater, or (3) Rayleigh fractionation in both the HCO_3^- reservoir and the
394 calcite precipitated from it. These hypotheses remain to be demonstrated following detailed
395 chemical analyses of the EPF.

396 In the past decade, several authors examined geochemical records ($\delta^{18}O$, Sr/Ca, Mg/Ca,
397 U/Ca) of SST variability in corals from the tropical south west Pacific Ocean (e.g., Kilbourne et
398 al. (2004) and references therein). These long-lived organisms can be used to reconstruct SST
399 variations over several centuries. However, subannual SST reconstructions using corals are
400 problematic because of the absence of clear sub-annual growth bands (Risk and Pearce, 1992).
401 In most high resolution coral studies (e.g., Meibom et al., 2004), a chronology is developed by
402 assuming constant growth rates and measuring distance along a transect, even though corals are
403 known to exhibit highly variable daily growth rates (Risk and Pearce, 1992). In contrast, scallop
404 shells can provide short SST time series (on the order of a few years) with very high temporal
405 resolution (circa-daily), thus providing accurate estimates of the full range of environmental
406 conditions that these organisms experience while growing. Scallops are thus more likely to
407 record high frequency, extreme environmental events, at least as long as the stress induced does
408 not interfere with the scallop's growth. This characteristic is particularly useful for the
409 investigation of coral bleaching events. Moberg et al. (2005) pointed out the need for

 doi: 10.1016/j.gca.2006.10.017

multi-proxy approaches for accurate reconstruction of past seawater temperature variations, by combining long, low-frequency data sets (such as from corals) with high-frequency information (e.g., from scallop shell data). As a large edible species, ancient *C. radula* specimens are abundant at archaeological sites (J.-C. Galipaud, personal communication), and ancient shells may also be found by coring fossil reef or sand units. In this context, corals and scallops may become complementary tools for SST reconstructions in the tropical southwest Pacific.

 doi: 10.1016/j.gca.2006.10.017

Acknowledgements. We would like to express our gratitude to Sandrine Chifflet and Pierre Waigna (IRD New Caledonia) for their valuable help during the salinity:$\delta^{18}O_{water}$ calibration, as well as to Paul F. Dennis (University of East Anglia, England - $\delta^{18}O_{water}$ analyses), and to François Michaud (Université de Bretagne Occidentale, France - XRD analyses). We would also like to acknowledge Alexandre Ganachaud and David Varillon (IRD New Caledonia) for providing us temperature and salinity data around Nouméa over the period 1995-2003 (ZoNeCo programme). Special thanks to Nolwenn Coïc for her help in maps and the production of figures. This manuscript has greatly benefited from critical reviews and very helpful comments by Alfonso Mucci, Donna Surge, Ann Goewert and two anonymous reviewers. This work was supported by IRD, the Programme National Environnement Côtier (PNEC) and the ACI-PECTEN. It was part of a 3-year research program funded by IRD and the Région Bretagne. Contribution N°1016 of the IUEM, European Institute for Marine Studies (Brest, France).

 doi: 10.1016/j.gca.2006.10.017

REFERENCES

Andreasson F. P. and Schmitz B. (1996) Winter and summer temperatures of the early middle Eocene of France from *Turritella* $\delta^{18}O$ profiles. *Geology* **24**, 1067-1070.

Andreasson F. P. and Schmitz B. (1998) Tropical Atlantic seasonal dynamics in the early middle Eocene from stable oxygen and carbon isotopes profiles of mollusk shells. *Paleoceanography* **13**, 183-192.

Andreasson F. P. and Schmitz B. (2000) Temperature seasonality in the early middle Eocene North Atlantic region: Evidence from stable isotope profiles of marine gastropod shells. *Geol. Soc. Am. Bull.* **112**, 628-640.

Barbin V., Schein E., Roux M., Decrouez D. and Ramseyer K. (1991) Stries de croissance révélées par cathodoluminescence dans la coquille de *Pecten maximus* (L.) récent de la rade de Brest (Pectinidae, Bivalvia). *Geobios* **24**, 65-70.

Beck J. W., Edwards R. L., Ito E., Taylor F. W., Recy J., Rougerie F., Joannot P. and Henin C. (1992) Sea-surface temperature from coral skeletal strontium/calcium ratios. *Science* **257**, 644-647.

Bice K. L., Arthur M. A. and Marincovich, Jr., L. (1996) Late Paleocene Arctic Ocean shallow-marine temperatures from mollusc stable isotopes. *Paleoceanography* **11**, 241-249.

Chauvaud L., Thouzeau G. and Paulet Y.-M. (1998) Effects of environmental factors on the daily growth rate of *Pecten maximus* juveniles in the Bay of Brest (France). *J. Exp. Mar. Biol. Ecol.* **227**, 83-111.

Chauvaud L., Lorrain A., Dunbar R. B., Paulet Y.-M., Thouzeau G., Jean F., Guarini J.-M. and Mucciarone D. (2005) Shell of the Great Scallop *Pecten maximus* as a high-frequency archive of paleoenvironmental change. *Geochem. Geophys. Geosystems* **6**, Q08001. doi:10.1029/2004GC000890.

Coplen T. B., Kendall C. and Hopple J. (1983) Comparison of stable isotope reference samples. *Nature* **302**, 236-238.

456 Corrège T., Gagan M. K., Beck J. W., Burr G. S., Cabioch G. and Le Cornec F. (2004)
457 Interdecadal variation in the extent of South Pacific tropical waters during the Younger
458 Dryas event. *Nature* **428**, 927-929.

459 Craig H. (1965) The measurement of oxygen isotope paleotemperatures. In *Stable isotopes in*
460 *oceanographic studies and paleotemperatures* (ed. E. Tongiorgi). Consiglio Nazionale
461 delle Ricerche, Laboratorio di Geologia Nucleare, Pisa. pp. 161-182.

462 Craig H. and Gordon L. I. (1965) Deuterium and oxygen 18 variations in the ocean and marine
463 atmosphere. In *Stable isotopes in oceanographic studies and paleotemperatures* (ed. E.
464 Tongiorgi). Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa.
465 pp. 9-130.

466 Crenshaw M. A. (1972) The inorganic composition of molluscan extrapallial fluid. *Biol. Bull.*
467 **143**, 506-512.

468 Dunbar R. B. and Cole J. E. (1999) *Annual Records of Tropical Systems*. PAGES Workshop
469 Report, Series 99-1, Bern, Switzerland.

470 Dutton A. L., Lohmann K. C. and Zinsmeister W. J. (2002) Stable isotope and minor element
471 proxies for Eocene climate of Seymour Island, Antarctica. *Paleoceanography* **17**, 1016.
472 doi:10.1029/2000PA000593.

473 Elliot M., deMenocal P. B., Linsley B. K. and Howe S. S. (2003) Environmental controls on the
474 stable isotopic composition of *Mercenaria mercenaria*: Potential application to
475 paleoenvironmental studies. *Geochem. Geophys. Geosystems* **4**, 1056.
476 doi:10.1029/2002GC000425.

477 Epstein S. and Mayeda T. (1953) Variation of O^{18} content of waters from natural sources.
478 *Geochim. Cosmochim. Acta* **4**, 213-224.

479 Epstein S., Buchsbaum R., Lowenstam H. A. and Urey H. C. (1953) Revised carbonate-water
480 isotopic temperature scale. *Bull. Geol. Soc. Am.* **64**, 1315-1326.

481 Gillikin D. P., Lorrain A., Navez J., Taylor J. W., André L., Keppens E., Baeyens W. and
482 Dehairs F. (2005) Strong biological controls on Sr/Ca ratios in aragonitic marine bivalve
483 shells. *Geochem. Geophys. Geosystems* **6**, Q05009. doi:10.1029/2004GC000874.

 doi: 10.1016/j.gca.2006.10.017

484 Hickson J. A., Johnson A. L. A., Heaton T. H. E. and Balson P. S. (2000) Late Holocene
485 environment of the southern North Sea from the stable isotopic composition of Queen
486 Scallop shells. *Palaeontol. Electronica* **3**, 1-11.
487 Kendall C. and Caldwell E. A. (1998) Chapter 2: Fundamentals of isotope geochemistry. In
488 *Isotope tracers in catchment hydrology* (eds. C. Kendall and J. J. McDonnell). Elsevier
489 Science B.V., Amsterdam. pp. 51-86.
490 Kennedy H., Richardson C. A., Duarte C. M. and Kennedy D. P. (2001) Oxygen and carbon
491 stable isotopic profiles of the fan mussel, *Pinna nobilis*, and reconstruction of sea surface
492 temperatures in the Mediterranean. *Mar. Biol.* **139**, 1115-1124.
493 Kilbourne K. H., Quinn T. M., Taylor F. W., Delcroix T. and Gouriou Y. (2004) El
494 Niño-Southern Oscillation-related salinity variations recorded in the skeletal
495 geochemistry of a *Porites* coral from Espiritu Santo, Vanuatu. *Paleoceanography* **19**,
496 PA4002. doi:10.1029/2004PA001033.
497 Kim S.-T. and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in
498 synthetic carbonates. *Geochim. Cosmochim. Acta* **61**, 3461-3475.
499 Kim S.-T., Hillaire-Marcel C. and Mucci A. (2006) Mechanisms of equilibrium and kinetic
500 oxygen isotope effects in synthetic aragonite at 25°C. *Geochim. Cosmochim. Acta.* **70**,
501 A318.
502 Kirby M. X., Soniat T. M. and Spero H. J. (1998) Stable isotope sclerochronology of
503 Pleistocene and Recent oyster shells (*Crassostrea virginica*). *Palaios* **13**, 560-569.
504 Krantz D. E., Jones D. S. and Williams D. F. (1984) Growth rates of the sea scallop,
505 *Placopecten magellanicus*, determined from the $^{18}O/^{16}O$ record in shell calcite. *Biol. Bull.*
506 **167**, 186-199.
507 Krantz D. E., Williams D. F. and Jones D. S. (1987) Ecological and paleoenvironmental
508 information using stable isotope profiles from living and fossil molluscs. *Palaeogeogr.*
509 *Palaeoclimatol. Palaeoecol.* **58**, 249-266.

Lefort Y. (1994) Growth and mortality of the tropical scallops: *Annachlamys flabellata* (Bernardi), *Comptopallium radula* (Linne) and *Mimachlamys gloriosa* (Reeve) in southwest lagoon of New Caledonia. *J. Shellfish. Res.* **13**, 539-546.

Lefort Y. and Clavier J. (1994) Reproduction of *Annachlamys flabellata, Comptopallium radula* and *Mimachlamys gloriosa* (Mollusca: Pectinidae) in the south-west lagoon of New Caledonia. *Aquat. Living Resour.* **7**, 39-46.

McConnaughey T. (1989) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochim. Cosmochim. Acta* **53**, 151-162.

McCrea J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849-857.

Meibom A., Cuif J.-P., Hillion F., Constantz B. R., Juillet-Leclerc A., Dauphin Y., Watanabe T. and Dunbar R. B. (2004) Distribution of magnesium in coral skeleton. *Geophys. Res. Lett.* **31**, L23306. doi:10.1029/2004GL021313.

Mickler P. J., Banner J. L., Stern L., Asmerom Y., Edwards R. L. and Ito E. (2004) Stable isotope variations in modern tropical speleothems: Evaluating equilibrium vs. kinetic isotope effects. *Geochim. Cosmochim. Acta* **68**, 4381-4393.

Mitchell L., Fallick A. E. and Curry G. B. (1994) Stable carbon and oxygen isotope compositions of mollusc shells from Britain and New Zealand. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **111**, 207-216.

Moberg A., Sonechkin D. M., Holmgren K., Datsenko N. M. and Karlén W. (2005) Highly variable Northern Hemisphere temperatures reconstructed from low- and high-resolution proxy data. *Nature* **433**, 613-617.

Owen R., Kennedy H. and Richardson C. (2002a) Experimental investigation into partitioning of stable isotopes between scallop (*Pecten maximus*) shell calcite and sea water. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **185**, 163-174.

Owen R., Kennedy H. and Richardson C. (2002b) Isotopic partitioning between scallop shell calcite and seawater: Effect of shell growth rate. *Geochim. Cosmochim. Acta* **66**, 1727-1737.

 doi: 10.1016/j.gca.2006.10.017

538 Pannella G. and MacClintock C. (1968) Biological and environmental rhythms reflected in
539 molluscan shell growth. *J. Paleontol.* **42**, 64-80.
540 Quinn T. M. and Sampson D. E. (2002) A multiproxy approach to reconstructing sea surface
541 conditions using coral skeleton geochemistry. *Paleoceanography* **17**, 1062.
542 doi:10.1029/2000PA000528.
543 Quinn T. M., Crowley T. J. and Taylor F. W. (1996a) New stable isotope results from a
544 173-year coral from Espiritu Santo, Vanuatu. *Geophys. Res. Lett.* **23**, 3413-3416.
545 Quinn T. M., Taylor F. W., Crowley T. J. and Link S. M. (1996b) Evaluation of sampling
546 resolution in coral stable isotope records: A case study using records from New Caledonia
547 and Tarawa. *Paleoceanography* **11**, 529-542.
548 Quinn T. M., Crowley T. J., Taylor F. W., Henin C., Joannot P. and Join Y. (1998) A
549 multicentury stable isotope record from a New Caledonia coral: Interannual and decadal
550 sea surface temperature variability in the southwest Pacific since 1657 A.D.
551 *Paleoceanography* **13**, 412-426.
552 Risk M. J. and Pearce T. H. (1992) Interference imaging of daily growth bands in massive
553 corals. *Nature* **358**, 572-573.
554 Rohling E. J. and Bigg G. R. (1998) Paleosalinity and $\delta^{18}O$: A critical assessment. *J. Geophys.*
555 *Res. Oceans* **103**, 1307-1318.
556 Roux M., Schein E., Rio M., Davanzo F. and Filly A. (1990) Enregistrement des paramètres du
557 milieu et des phases de croissance par les rapports $^{18}O/^{16}O$ et $^{13}C/^{12}C$ dans la coquille de
558 *Pecten maximus* (Pectinidae, Bivalvia). *C.R. Adac. Sci. III* **310**, 385-390.
559 Sharp Z. D. (2006) *Principles of stable isotope geochemistry*. Prentice Hall, Upper Saddle
560 River.
561 Spero H. J., Bijma J., Lea D. W. and Bemis B. E. (1997) Effect of seawater carbonate
562 concentration on foraminiferal carbon and oxygen isotopes. *Nature* **390**, 497-500.
563 Surge D., Lohmann K. C. and Dettman D. L. (2001) Controls on isotopic chemistry of the
564 American oyster, *Crassostrea virginica*: implications for growth patterns. *Palaeogeogr.*
565 *Palaeoclimatol. Palaeoecol.* **172**, 283-296.

 doi: 10.1016/j.gca.2006.10.017

566 Tan F. C., Cai D. and Roddick D. L. (1988) Oxygen isotope studies on sea scallops,
567 *Placopecten magellanicus*, from Browns Bank, Nova Scotia. *Can. J. Fish. Aquat. Sci.* **45**,
568 1378-1386.
569 Thébault J., Chauvaud L., Clavier J., Fichez R. and Morize E. (2006) Evidence of a 2-day
570 periodicity of striae formation in the tropical scallop *Comptopallium radula* using calcein
571 marking. *Mar. Biol.* **149**, 257-267.
572 Tripati A., Zachos J., Marincovich, Jr., L. and Bice K. (2001) Late Paleocene Arctic coastal
573 climate inferred from molluscan stable and radiogenic isotope ratios. *Palaeogeogr.*
574 *Palaeoclimatol. Palaeoecol.* **170**, 101-113.
575 Urey H. C. (1947) The thermodynamic properties of isotopic substances. *J. Chem. Soc.* 562-
576 581.
577 Wada K. and Fujinuki T. (1976) Biomineralization in bivalve molluscs with emphasis on the
578 chemical composition of the extrapallial fluid. In *The mechanisms of mineralization in the*
579 *invertebrates and plants* (eds. N. Watabe and K. M. Wilbur). University of South
580 Carolina Press, Columbia. pp. 175-190.
581 Watanabe T., Gagan M. K., Corrège T., Scott-Gagan H., Cowley J. and Hantoro W. S. (2003)
582 Oxygen isotope systematics in *Diploastrea heliopora*: New coral archive of tropical
583 paleoclimate. *Geochim. Cosmochim. Acta* **67**, 1349-1358.
584 Wheeler A. P., Blackwelder P. L. and Wilbur K. M. (1975) Shell growth in the scallop
585 *Argopecten irradians*. I. Isotope incorporation with reference to diurnal growth. *Biol.*
586 *Bull.* **148**, 472-482.
587 Wilbur K. M. and Saleuddin A. S. M. (1983) Shell formation. In *The Mollusca - Volume 4:*
588 *Physiology - Part 1* (eds. A. S. M. Saleuddin and K. M. Wilbur). Academic Press, New
589 York. pp. 235-287.
590 Wrenn S. L. (1972) Daily increment formation and synchronization in the shell of the bay
591 scallop. *Am. Zool.* **12**, 32.
592 Zeebe R. E. (1999) An explanation of the effect of seawater carbonate concentration on
593 foraminiferal oxygen isotopes. *Geochim. Cosmochim. Acta* **63**, 2001-2007.

The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

TABLES

Table 1. Summary of some previous $\delta^{18}O$:temperature relationships calibrated for inorganically precipitated calcite and for calcitic molluscs. Oxygen isotope compositions of calcite (δ_c) and water (δ_w) are expressed relative to VPDB and VSMOW, respectively.

Reference	Source	$t(°C) = A + B(\delta_c - \delta_w) + C(\delta_c - \delta_w)^2$			Temperature range
		A	*B*	*C*	
Kim and O'Neil (1997)[a]	Inorganic	14.97	-4.97		10 - 40 °C
Owen et al. (2002a)[a]	Mollusc (*Pecten maximus*)	17.15	-3.99		10 - 17 °C
Chauvaud et al. (2005)	Mollusc (*Pecten maximus*)	14.84	-3.75		9 - 18 °C
Sharp (2006)[b]	Molluscs	15.75	-4.30	0.14	7 - 29.5 °C

(a) Rewritten in a form appropriate for comparison
(b) After Epstein et al. (1953) and Craig (1965)

The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

Table 2. Multiple linear regression between *Comptopallium radula* $\delta^{18}O_{shell\ calcite}$, temperature, salinity, and shell growth rate in 2002-2003, considering or not shell growth rate.

	Estimate	Std. error	T	*p*
	Shell growth rate considered [a]			
Intercept	84.66	18.77	4.511	< 0.001
Temperature (t)	-3.200	0.733	-4.363	< 0.001
Salinity (S)	-2.241	0.527	-4.253	< 0.001
Growth rate (GR)	-0.016	0.017	-0.908	0.365
t*S	0.084	0.021	4.056	< 0.001
t*GR	0.0003	0.0001	2.193	0.029
S*GR	0.0003	0.0005	0.548	0.584
	Shell growth rate not considered [b]			
Intercept	77.98	18.45	4.227	< 0.001
Temperature (t)	-3.030	0.727	-4.170	< 0.001
Salinity (S)	-2.103	0.522	-4.027	< 0.001
t*S	0.081	0.021	3.937	< 0.001

(a) Multiple r^2: 0.705; adjusted r^2: 0.697; F-statistic: 86.68 on 6 and 218 DF; *p*-value: < 0.001.
(b) Multiple r^2: 0.694; adjusted r^2: 0.690; F-statistic: 166.8 on 3 and 221 DF; *p*-value: < 0.001.

The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

Table 3. Parameters of the $\delta^{18}O$:temperature relationships (OLS regressions) calculated for each of the six shells separately, then for the shells of each study site separately. Also shown are the *p*-values resulting from the "comparison of regression lines" procedure.

Model fitting results: $t(°C) = A + B\ (\delta^{18}O_{shell\ calcite\ VPDB} - \delta^{18}O_{water\ VSMOW})$							**Test for equality of slopes**			
Shell	***n***	***p***	***r²***	***A***	***B***	**MAE**	**Source**	***p***	**Source**	***p***
SM1	38	< 0.001	0.748	19.45	-4.03	0.8	SM1			
SM2	34	< 0.001	0.764	18.70	-4.04	0.8	SM2	0.589	SM1	
SM3	40	< 0.001	0.650	19.89	-3.53	0.8	SM3		SM2	
BK1	40	< 0.001	0.490	20.28	-3.86	1.2	BK1		SM3	0.447
BK2	37	< 0.001	0.655	20.10	-3.73	0.9	BK2	0.331	BK1	
BK3	36	< 0.001	0.536	21.42	-2.88	1.0	BK3		BK2	
									BK3	
SM_{pooled}	112	< 0.001	0.718	19.22	-3.95	0.8	SM_{pooled}	0.127		
BK_{pooled}	113	< 0.001	0.539	20.77	-3.37	1.1	BK_{pooled}			

The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

FIGURE CAPTIONS

Fig. 1. a) Photograph of the upper surface of the left valve of *Comptopallium radula*. The maximal growth axis is indicated by the white arrow. b) Image (scanning electron microscopy) of striae taken along the maximal growth axis. These striae have been demonstrated to form with a 2-day periodicity (Thébault et al., 2006). Three shell samples drilled for isotopic analysis can be readily seen. Each sample contains material from two striae and is separated from the next one by two striae.

Fig. 2. Scallop sampling locations in the southwest lagoon of New Caledonia. Dashed line delimits the area of water sampling for $\delta^{18}O_{water}$:salinity calibration.

Fig. 3. Variations of $\delta^{18}O_{shell\ calcite}$ (black points), bottom-water temperature (5-day moving average; black line) and shell growth rate (grey area) in the six studied *Comptopallium radula* specimens, from August 2002 to July 2003.

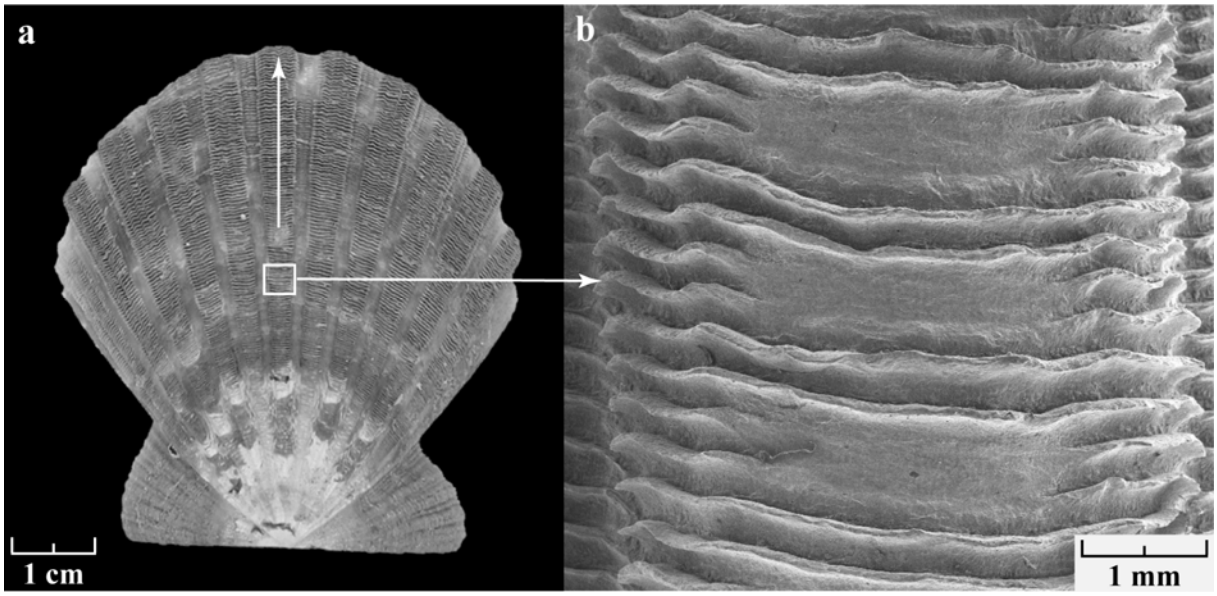
Fig. 4. Relationship between bottom-water temperature (°C) and ($\delta^{18}O_{shell\ calcite}$ - $\delta^{18}O_{water}$) where $\delta^{18}O_{shell\ calcite}$ and $\delta^{18}O_{water}$ are expressed on the VPDB and VSMOW scales, respectively. Also represented are the linear regression model and its equation.

Fig. 5. Comparison of temperature predictions using our new *Comptopallium radula* $\delta^{18}O$:temperature relationship and previously published paleotemperature equations. The position of our equation with respect to the theoretical equilibrium equation of Kim and O'Neil (1997) indicates that the shell of *Comptopallium radula* is not formed in isotopic equilibrium with seawater.

Fig. 6. Relationship between $\delta^{18}O_{shell\ calcite}$ and $\delta^{13}C_{shell\ calcite}$ of the 6 juvenile scallops (OLS regression: $n = 225$, $r^2 = 0.206$, $p < 0.001$).

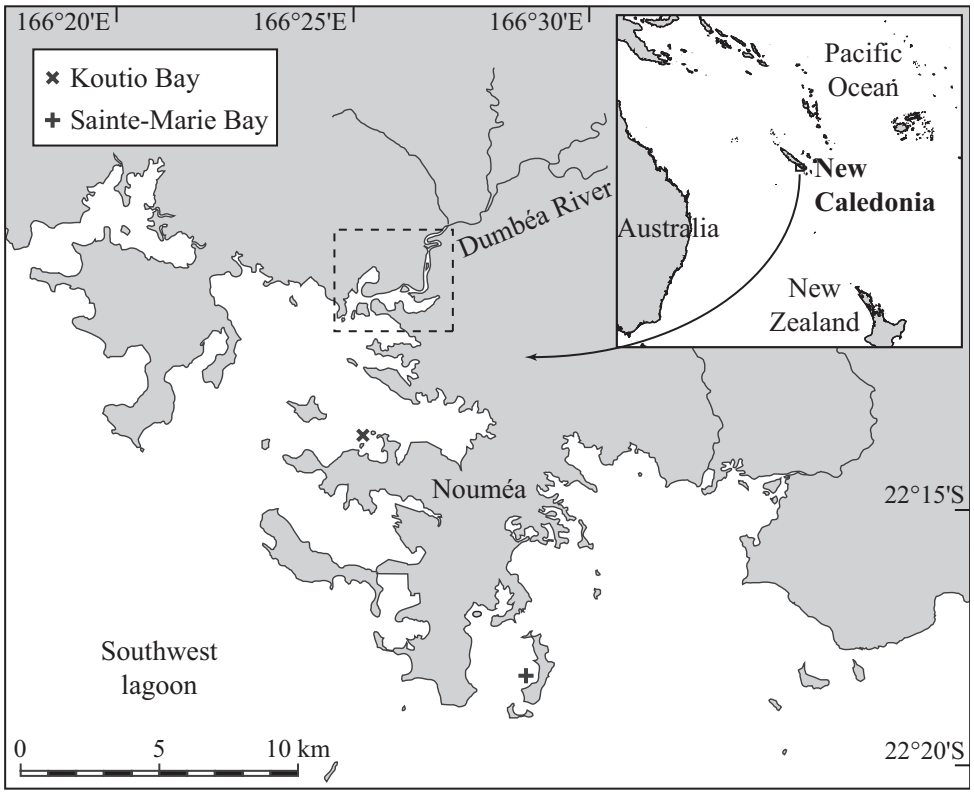
 doi: 10.1016/j.gca.2006.10.017

Figure 1



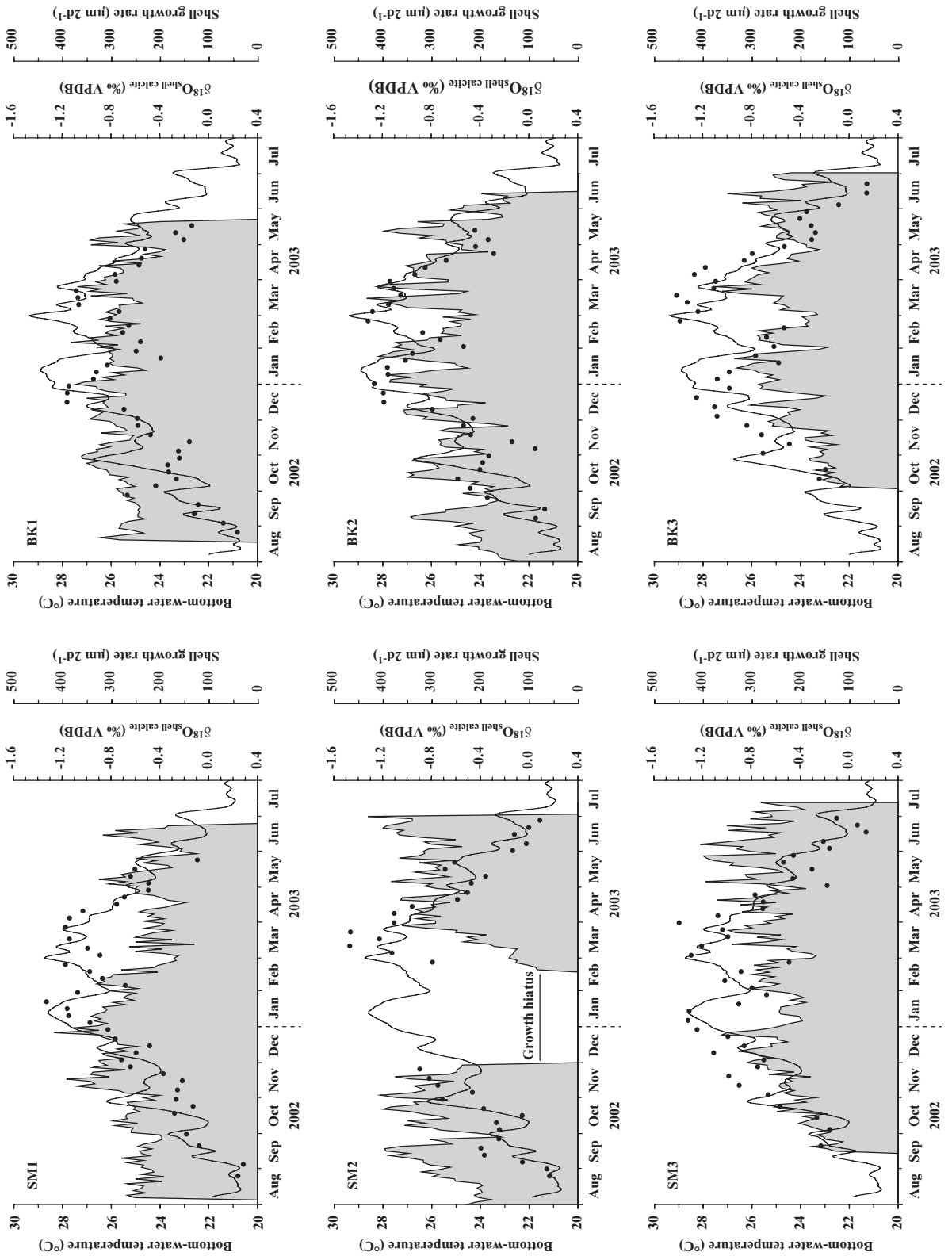
The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

Figure 2



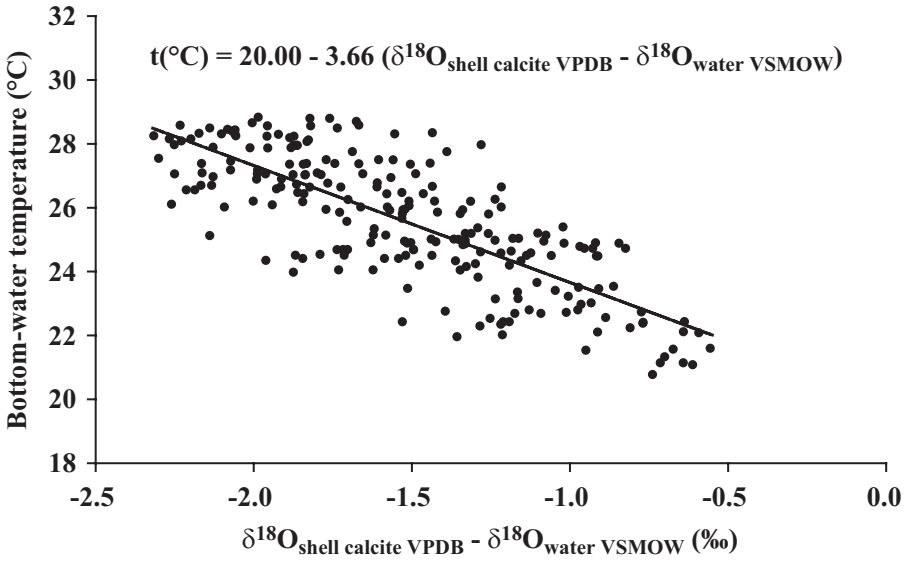
The original publication is available at www.sciencedirect.com doi: 10.1016/j.gca.2006.10.017

Figure 3



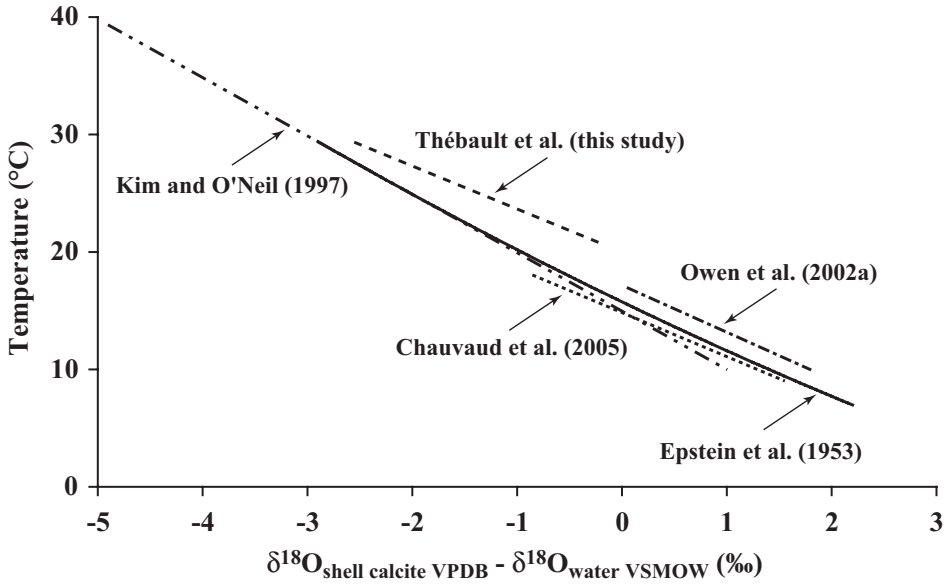
 doi: 10.1016/j.gca.2006.10.017

Figure 4



 doi: 10.1016/j.gca.2006.10.017

Figure 5



 doi: 10.1016/j.gca.2006.10.017

Figure 6